



Short communication

Trimethyl phosphite as an electrolyte additive for high-voltage lithium-ion batteries using lithium-rich layered oxide cathode

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HIGHLIGHTS

- Trimethyl phosphite (TMP) is investigated as a high-voltage electrolyte additive.
- Addition of 1% TMP can enhance capacity retention and rate capability.
- The passivating interphase is built by TMP on the $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ cathode.

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ABSTRACT

Lithium-rich layered oxide cathode is a promising high-capacity cathode material for high-energy lithium-ion batteries. However, to achieve its high capacity, the development of high-voltage electrolytes is essential. In this work, trimethyl phosphite (TMP) is investigated as an electrolyte additive for high-voltage lithium-ion batteries using $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ cathode. When 1% TMP is introduced into the electrolyte, cycling performance and rate capability of the $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ cathode are improved significantly. The $\text{Li}/\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ cell with the TMP-containing electrolyte exhibits high capacity retention of 81.3% after 100 cycles and good rate capability of 150 mA h g^{-1} at 5 C and 90 mA h g^{-1} at 10 C, while the capacity of the cell without TMP is 48 mA h g^{-1} at 5 C. Based on the measurements on impedance spectra and thermal stability, it is concluded that TMP can effectively deactivate the catalyzing effect of some transition metal ions on the surface of the $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ cathode.

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1. Introduction

Lithium-rich layered oxide cathode materials, represented by $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ ($M = \text{Ni}, \text{Co}, \text{Mn}$), have been intensively studied as high capacity cathode materials for lithium-ion batteries [1–10]. They usually can deliver a reversible capacity of $\sim 250 \text{ mA h g}^{-1}$ between 2.0 and 4.8 V, which is quite attractive to high-energy lithium-ion batteries for electric vehicle applications. Such a large capacity cannot be achieved until the cathode is charged to an upper cut-off voltage of 4.6–4.8 V in order to activate Li_2MnO_3 component. The high voltage is a rigorous challenge to the state-of-the-art electrolyte. Although the organic carbonate solvents in the

electrolyte usually have quite high anodic potentials exceeding 5 V on inert electrodes, they seldom keep stable enough at potentials only above 4.4 V during long-term cycling on the active electrode [11]. The main reason is that the carbonate solvents are apt to be catalyzed to decompose by strongly oxidative charged electrode. These aggressive side reactions are responsible for the large initial irreversible capacity loss and distinct capacity fading during cycling.

In order to make lithium-rich layered oxide cathode materials commercially available, it is necessary to improve the stability of electrolyte on these high-voltage cathodes. There are two ways to make the electrolyte compatible with the high-voltage cathodes. One is to replace the carbonate-based electrolytes with novel electrolyte systems intrinsically exhibiting high anodic stability. Succinonitrile and sulfone-based electrolytes have been investigated in the 5 V $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cells and LiCoO_2 cells with charge cut-off voltage of 4.5 V [12,13]. The other way is to make the

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carbonate-based electrolytes dynamically stable to the high-voltage cathodes. At most time, some additives were used to deactivate the active “catalytic” centers on the cathode surface in order to remain inert for the bulk electrolyte [14–16]. Lucht *et al.* reported that inorganic additives including lithium bisoxalatoborate, lithium difluorooxalatoborate and tetramethoxy titanium could effectively passivate the $\text{Li}_{1.17}\text{Mn}_{0.58}\text{Ni}_{0.25}\text{O}_2$ cathode and result in a decrease in detrimental electrolyte oxidative decomposition reactions on the cathode surface [15]. After Xu *et al.* introduced 1% tris(hexafluoroisopropyl) phosphate into the carbonate-based electrolyte, the cycling performance of 5 V lithium-ion batteries had been improved evidently [16]. Basically, exploitation of high-voltage electrolyte additives is a greatly promising route in support of the high-energy lithium-ion batteries using the lithium-rich layered oxide cathodes.

Trimethyl phosphite (TMP) has been investigated as an effective electrolyte additive to improve the safety characteristics of lithium-ion batteries in our previous report [17,18]. In this paper, we explored the feasibility of TMP as an electrolyte additive in support of high-voltage lithium-ion batteries using the cathode material $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$, which can be rewritten in two-component notation as $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$. The impact of TMP on cycling performance and rate capability of the $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ cathode was investigated. Impedance spectra and thermal stability were measured to deduce the effect of TMP on the cathode/electrolyte interphase.

2. Experimental

2.1. Materials preparation and cell assembly

$\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ was prepared by a co-precipitation method, as described previously [19]. As-purchased TMP was purified with a distillation step under vacuum and dried before use over molecular sieves (4 Å). An electrolyte of 1 M LiPF_6 in a mixture of 1:1 (w/w) ethylene carbonate (EC) and diethyl carbonate (DEC) was selected as a baseline electrolyte. Different contents of TMP were added in the baseline electrolyte in an argon-filled glove box (MBraun).

Electrochemical properties of the $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ cathode material were evaluated by using 2032-type coin cells assembled in the glove box. In order to make the $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ electrode laminate, a slurry containing 84 wt.% active material, 8 wt.% acetylene black and 8 wt.% polyvinylidene fluoride (PVDF) dispersed in N-methyl-2-pyrrolidinone (NMP) was cast onto an aluminum current collector. After vacuum drying at 70 °C, the laminate was punched into discs (14 mm) for assembling the coin cells. The mass loading in the electrode was controlled at about 8 mg cm^{-2} . Celgard 2400 microporous polypropylene membrane was used as separator. Highly pure lithium foil was used as the counter electrode and reference electrode for the cell assembly.

2.2. Measurements on electrochemical properties and thermal stability

Electrochemical stability of the electrolytes on the $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ electrodes was measured by linear sweep voltammetry (LSV) from open circuit potential to 6 V at a scan rate of 0.2 mV s^{-1} . Ac impedance measurements were performed over the frequency range of 100 kHz to 1 mHz at an amplitude of 10 mV. Both measurements were carried out in the Li/Li $_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ cells on a CHI 604D electrochemical workstation. The cell performance of $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ was evaluated on a multi-channel battery cycler (Neware BTS2300). All the cells were cycled between 2.5 and 4.8 V at a current rate of 0.1 C (1 C = 200 mA g^{-1}) for the initial three cycles. Then the cycling tests were performed at

a current rate of 0.5 C in the constant current–constant voltage (CC–CV) charge mode and constant current (CC) discharge mode between 2.5 and 4.6 V. The internal resistance of the cells was also measured by a current interruption technique. This was done by cutting off the current intermittently for 1 min through the process of charge and recording the voltage change after interruption. Thus, the dc impedance of a cell (R_{dc}) can be calculated as $R_{dc} = \Delta U / \Delta I$, where ΔU is the difference between the voltage of before and after the 1-min interruption [20]. All the testing above was performed in room temperature.

Thermal stability of the coexisting systems of $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ cathode and electrolyte was evaluated by using a Calvet-type calorimeter (Setaram C80). 23 mg cathode material and 50 mg electrolyte were placed in a high-pressure stainless steel vessel with dry argon atmosphere. The measurement was performed at a heating rate of 0.2 °C min^{-1} from room temperature to 300 °C, and the C80 calculations were based on the weight of the electrolyte. More details can be found in our previous report [21].

2.3. Calculation details

Based on Faraday's law, the oxidation potential of TMP vs. Li/Li⁺ can be calculated from the following formula:

$$E_0 = -[G_0(\text{TMP}) - G_0(\text{TMP}^+)]/e - 1.46 \text{ V} \quad (1)$$

The calculation of TMP's oxidation potential was performed by using the Gaussian03 program package [22]. The structures of TMP and TMP^+ were fully optimized by B3LYP method using 6-311++G(d,p) basis set. The polarizable continuum model (PCM) model was used in our calculations, since it can produce reasonable results in describing solvation effects on redox potentials in the electrolyte. Herein, the solvent radius is fixed to be 5.0 Å and dielectric constant to be 60.0 as reported by Dahn [23].

3. Results and discussion

In the TMP molecule, the oxidation number of phosphorous is three (III) and the phosphorous atom has a lone pair. Along with one electron lost, TMP can be oxidized into TMP^+ . After the TMP and TMP^+ structures were fully optimized, their standard free energies were calculated. Based on formula (1), the oxidation potential of TMP was calculated to be 4.93 V, which is lower than the oxidation potentials of EC and DEC. Therefore, TMP should be preferential to oxidize on the charged $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ than EC and DEC.

Fig. 1 shows the LSV curves of the electrolyte with or without 1% TMP on the $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ electrode. Both the curves contain three anodic peaks at 4.0 V, 4.6 V and 5.3 V, respectively. The first peak at 4.0 V is associated predominantly with Ni oxidation from Ni^{2+} to Ni^{4+} and Co oxidation from Co^{3+} to Co^{4+} , and the peak at 4.6 V is related to the electrochemical activation reaction of Li_2MnO_3 to MnO_2 with LiO stripped [24,25]. The last peak at 5.3 V is quite weak, which is resulted from the oxidation of the electrolyte on the high-voltage electrode. There is negligible difference between the two curves when the voltage is below 4.9 V. However, at the high potential region, the onset oxidative potential of the electrolyte with TMP is about 4.9 V, which is lower than 5.1 V of the baseline electrolyte. Moreover, the oxidative peak of the electrolyte with TMP is higher and broader than that of the electrolyte without TMP. The possible reason is that TMP is apt to oxidative decomposition in a more aggressive way. The onset oxidative potential of TMP is about 4.9 V, which is in good agreement with the calculation result (4.93 V).

The cell performance of Li/Li $_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ cells containing the electrolytes with and without TMP is shown in Fig. 2. All

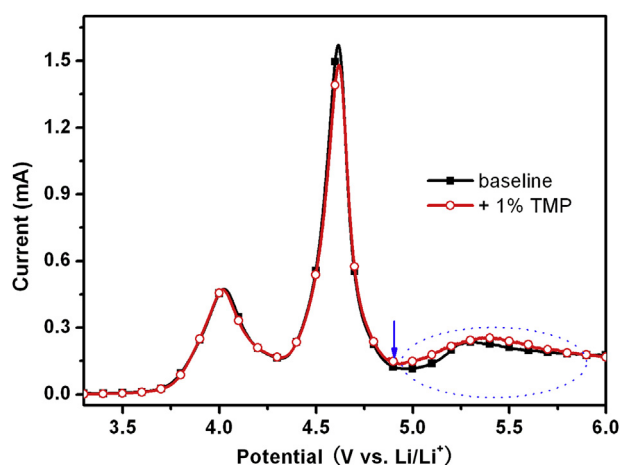


Fig. 1. LSV curves of the electrolyte with or without 1% TMP on the $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ electrode. Scan rate: 0.2 mV s^{-1} .

the cells with the three electrolytes have the comparative discharge capacity of $\sim 270 \text{ mA h g}^{-1}$ but distinctly different charge capacity (Fig. 2a). Thus, their coulombic efficiencies are different. The cell using the baseline electrolyte has an initial coulombic efficiency of 88.2%. After TMP was added into the electrolyte, the coulombic

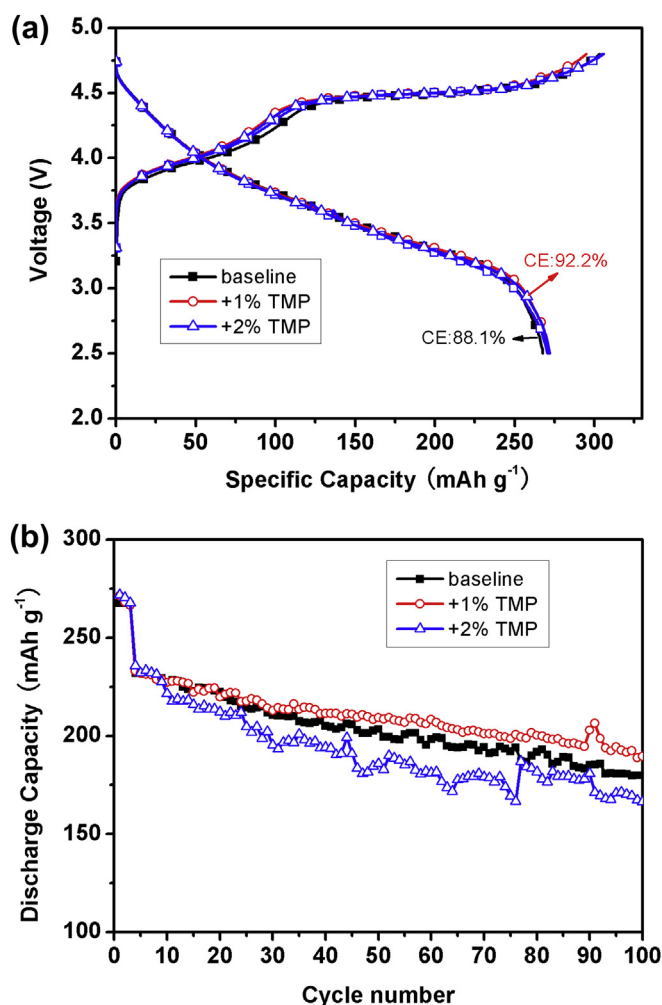


Fig. 2. The initial voltage profiles (a) and cycling performance (b) of $\text{Li}/\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ cells using different electrolytes.

efficiency increased slightly, such as 92.0% for the electrolyte containing 1% TMP and 89.1% for the electrolyte containing 2% TMP. The increased coulombic efficiency probably results from the depressed side reactions between electrolyte and charged $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ cathode. But the cell using the electrolyte with 2% TMP has a lower coulombic efficiency than that with 1% TMP. The possible reason for excess charge capacity is the oxidation decomposition of too much TMP on the cathode surface. Moreover, after more TMP was introduced into the electrolyte, e.g. 5% or 10%, the $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2/\text{Li}$ cells exhibited lower initial coulombic efficiency (72% for the electrolyte containing 5% TMP and 68% for the electrolyte containing 10% TMP). These results (not shown here) indicate that too much TMP is not stable on the high-voltage lithium-rich layered oxide cathode, which is obviously different from the things on the LiCoO_2 cathode [18]. Fig. 2b shows the cycling performance of $\text{Li}/\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ cells using different electrolytes. In the first three cycles, all the cells with different electrolytes were subjected to a preconditioning cycle at 0.1 C rate, and then cycled at 0.5 C. At the fourth cycle, the discharge capacities of the different cells are quite close to about 230 mA h g^{-1} at 0.5 C. However, at the 100th cycle, the residual discharge capacities are $179.9 \text{ mA h g}^{-1}$ for the baseline electrolyte, $189.5 \text{ mA h g}^{-1}$ for the electrolyte with 1% TMP and $166.5 \text{ mA h g}^{-1}$ for the electrolyte with 2% TMP, respectively. Based on the discharge capacity at the 4th cycle, the capacity retention of the cell using the baseline electrolyte is 77.5%. As for the cells with the electrolytes containing TMP, the capacity retentions at the 100th cycle are 81.3% for 1% TMP and 70.6% for 2% TMP, respectively. As compared with the baseline electrolyte, the cycling performance of the cell containing 1% TMP is improved, because the presence of TMP stabilizes the interphase between $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ cathode and electrolyte. It should be noted that the cell using 2% TMP shows poorer cycling stability than the cell using 1% TMP, suggesting that TMP as a high-voltage additive can only be used in a small concentration.

It is widely reported that the rate capability of lithium-rich layered oxide cathode is poor, which becomes one of main drawbacks of this material for the commercial utilization [26–28]. The poor rate capability is usually ascribed to the formation of a thick passivating film on the cathode surface owing to electrolyte oxidation at high potentials [29]. Fig. 3 shows rate capability of $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ in the baseline electrolyte and the electrolyte containing 1% TMP. There is negligible difference between the discharge capacities of the cells using the electrolytes with and without TMP at low current rates (0.1 C and 0.5 C). When the current

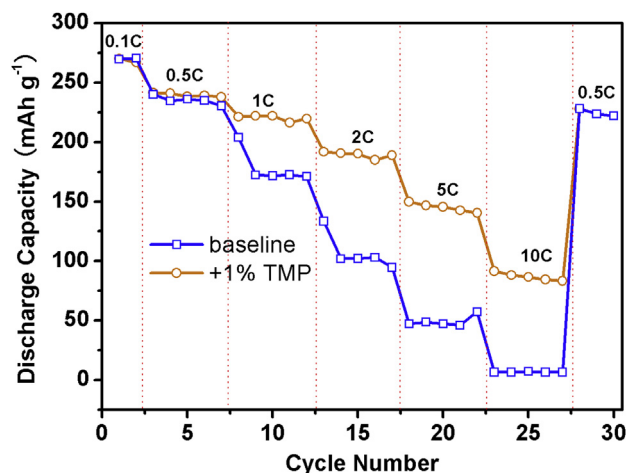


Fig. 3. Rate capability of $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ in the baseline electrolyte and the electrolyte containing 1% TMP.

rate increases to 1 C from 0.5 C, the discharge capacity of the cell using the baseline electrolyte rapidly drops to 172 mA h g^{-1} from 231 mA h g^{-1} , but that of the cell with 1% TMP remains 223 mA h g^{-1} . Along with the current rates increasing, the discharge capacities of the cell using the baseline electrolyte are 103 mA h g^{-1} at 2 C, 48 mA h g^{-1} at 5 C and less than 10 mA h g^{-1} at 10 C. However, for the cell with the electrolyte containing 1% TMP, the discharge capacities are obviously higher than those for the cell using the baseline electrolyte at the same current rates. At 2 C, 5 C and 10 C, the discharge capacities are 192 mA h g^{-1} , 150 mA h g^{-1} and 92 mA h g^{-1} , respectively. In addition, after the low current rate of 0.5 C was used again, the discharge capacities of both the cells can be restored.

As shown in Fig. 4, the dc resistance measurements show that the cell containing 1% TMP has the higher dc resistance than that with the baseline electrolyte, especially at the beginning of charging ($<4 \text{ V}$). Considering that there is no obvious difference in their LSV curves (Fig. 1) and the initial voltage profiles (Fig. 2a) during this period ($<4 \text{ V}$), we speculate that the high dc resistance does not come from the electrochemical reactions inspired by TMP molecule. It is most likely caused by electrostatic interaction between TMP and charged $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ cathode.

Effect of TMP on the cell performance of $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ cathode was understood from the ac impedance spectra further. Fig. 5 shows the Nyquist plots of the cells with the baseline electrolyte and the electrolyte containing 1% TMP. Each curve is composed of two overlapped semicircles in the high-to-medium frequency range and a straight line in the low frequency range. According to previous studies [30,31], the semicircle in the high frequency range can be ascribed to Li ion migration through the interphase film between electrode and electrolyte, while the semicircle in the medium frequency range is assigned to charge transfer reaction. From Fig. 5a, we can obviously find that the cell containing TMP exhibits a higher interphase resistance than that without TMP at the 3rd cycle, suggesting that an interphase film with high resistance has been built on the surface of the high-voltage $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ cathode. In contrary, the cell without TMP has a higher interphase resistance than that with TMP at the 10th cycle, even though the resistances of both cells increase obviously. As the cycle number increases, the interphase resistance of the cell without TMP rise drastically, probably along with the interphase film becomes thicker and thicker because of the continual oxidative decomposition of the electrolyte on the high-voltage cathode. From the results of ac impedance spectra, it can be deduced that both the interfacial layers are not completely compact so that the interfacial

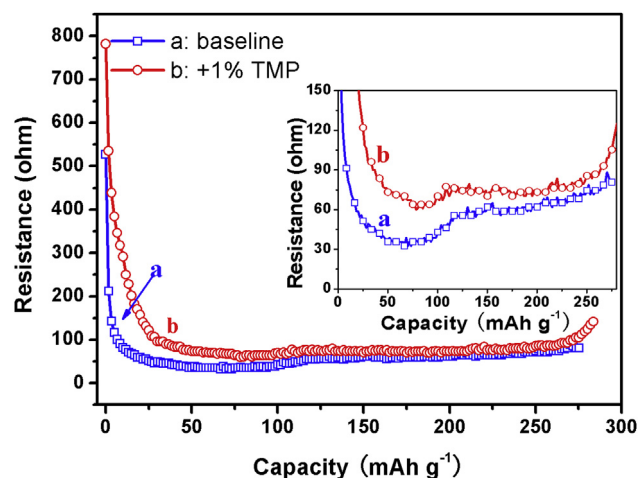


Fig. 4. Relationship between special capacity and dc resistance of the cells with the baseline electrolyte and the electrolyte containing 1% TMP.

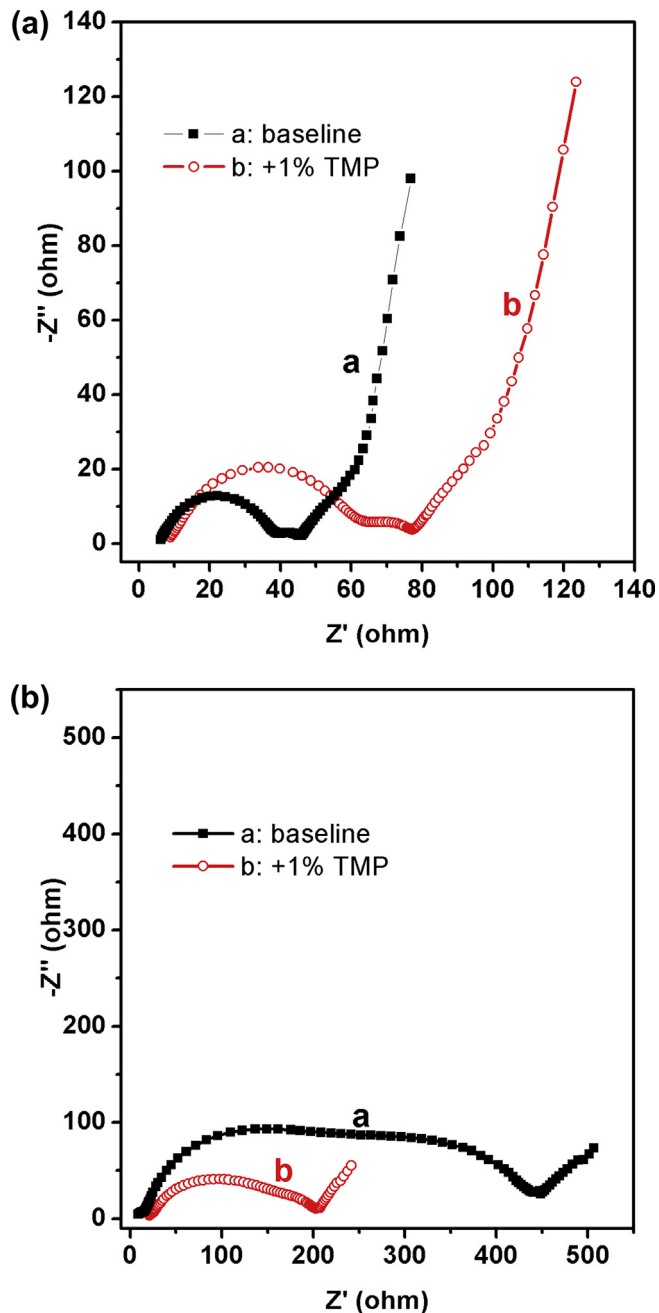


Fig. 5. Ac impedance spectra of cells using the baseline electrolyte and the electrolyte containing 1% TMP, (a) at the 3rd cycle (b) at the 10th cycle. The ac impedance was measured after the cells had been charged to 50% state of the charge and the cells been placed statically for about 30 min.

impedance is increasing ceaselessly, but it is likely that the interfacial layer formed in the TMP-containing electrolyte is relatively more compact and stable. The introduction of TMP into the electrolyte could effectively deactivate the catalyzing effect of some transition metal ions on the surface of the high-voltage electrode, so the rise of the interphase resistance is depressed to a certain extent. Therefore, suppression on the rise impedance during cycling by performing a passivating interphase is one of the main reasons for the improved cycling performance and rate capability of $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ in the TMP-containing electrolyte.

Fig. 6 shows the C80 heat flow curves of the charged $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ cathode materials with the corresponding electrolyte. As we reported previously [21], the maximal heat flow

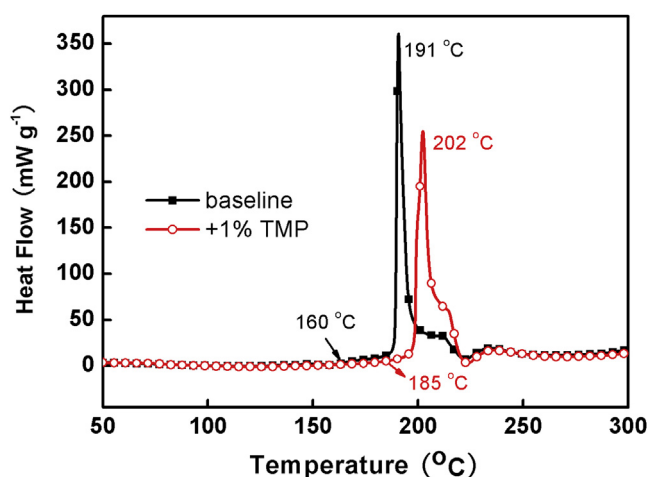


Fig. 6. C80 heat flow curves of coexistence systems of 50 mg electrolyte and 23 mg delithiated $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ cathode materials (charged to 4.6 V) at a heating rate of $0.2\text{ }^{\circ}\text{C min}^{-1}$.

and its corresponding temperature both have very important effect on the thermal stability of lithium-ion batteries. Herein, the main exothermic peak appears at $191\text{ }^{\circ}\text{C}$ with a high heat flow of 330 mW g^{-1} for the coexisting system of the charged $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ cathode materials and the baseline electrolyte. As for the TMP-containing system, the maximal heat flow is depressed to 224 mW g^{-1} and its corresponding temperature is postponed to $202\text{ }^{\circ}\text{C}$. In addition, the system without TMP has a lower onset exothermic temperature of $160\text{ }^{\circ}\text{C}$ than the system with TMP ($185\text{ }^{\circ}\text{C}$). In conclusion, all the C80 results support the viewpoint that introduction of only 1% TMP into electrolyte has significantly enhanced the thermal stability of the coexisting systems of charged $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ cathode and electrolyte. The main exothermic reactions between charged cathode and electrolyte are related to the catalytic properties of surface metal ions of the cathode [32,33]. Herein, TMP acts as a film-formation additive to build the passivating interphase on the surface of the $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ cathode, and then the passivating electrolyte/cathode interphase layer could deactivate the active “catalytic” centers. Therefore, the thermal stability of the charged $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ cathode and electrolyte had been enhanced by introduction of 1% TMP.

All the results above strongly suggest that 1% TMP can help to found a stable interphase on the $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ cathode. In our previous report, ex-situ FTIR analysis indicated that Li_xPO_y was an important surface film composition on the LiCoO_2 cathode in the electrolyte containing 5% TMP [18]. Herein, a similar reaction mechanism is acceptable on the $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ cathode. Only 1% TMP can even be oxidatively decomposed more drastically on the surface of high-voltage $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ cathode than 5% TMP on the LiCoO_2 cathode. That Li_xPO_y -containing interfacial passivation layer improved electrochemical performance and thermal stability of the $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ cathode.

4. Conclusions

Trimethyl phosphite (TMP) has been investigated as an electrolyte additive for high-voltage lithium-ion batteries using lithium-rich layered oxide cathode, $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$. After 1% TMP was introduced into the baseline electrolyte, the initial irreversible capacity loss of the $\text{Li}/\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ cell has been reduced and the capacity retention is elevated to 81.3% from 79.4% after 100 cycles. Especially, the rate capability has been improved evidently. The cell containing 1% TMP releases the

discharge capacities of 150 mA h g^{-1} at 5 C and 90 mA h g^{-1} at 10 C, respectively. Even though effect of TMP on the compatibility between lithium-rich layered oxide cathode and electrolyte has been confirmed in current work, some cell performance, for example the initial irreversible capacity and the cycling performance, should be optimized further for actual application.

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